

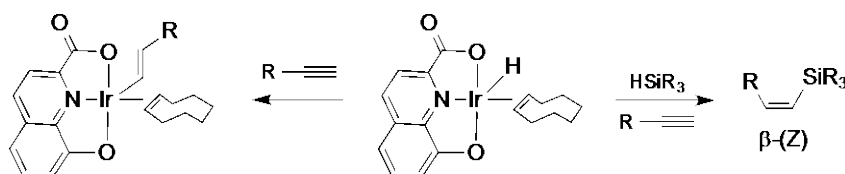
## MECHANISTIC INSIGHTS INTO THE HYDROSILYLATION OF TERMINAL ALKYNES CATALYZED BY A ONO-PINCER IRIIDIUM(III) HYDRIDE COMPOUND

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Transition-metal catalyzed hydrosilylation of terminal alkynes is the most straightforward and atom-economical methodology for the preparation of vinylsilanes, which are valuable synthetic intermediates [1]. The control of the regio- and stereoselectivity of the reaction is a key issue and therefore a deeper understanding of the reaction mechanisms is pivotal for the development of more active and selective catalytic systems. On the other hand, pincer ligands are valuable structural motifs for the design of transition-metal complexes for selective stoichiometric and catalytic transformations. In particular, O-based anionic pincer ligands have attracted significant attention for supporting high-oxidation-state metal complexes by modulating the electron density at the metal centre via a hard/hard interaction or  $\pi$ -donating effects. We have recently shown the potential of tridentate dianionic ONO pincer-type ligands for the design of unsaturated iridium(III) compounds which have shown catalytic activity in C–H activation/functionalization processes. [2]

The unsaturated hydrido iridium(III) compound  $[\text{IrH}(\kappa^3\text{-hqca})(\text{coe})]$  (hqca = 8-oxidoquinoline-2-carboxylate) is an efficient catalysts precursor for the hydrosilylation of a range of terminal alkynes with excellent yields and an outstanding  $\beta$ -(Z) selectivity for aliphatic alkynes. This species reacts with a range of terminal alkynes to give  $\eta^1$ -alkenyl complexes that are also competent for alkyne hydrosilylation.



The presence of a rigid dianionic ONO pincer-type ligand could facilitate the stabilization of  $\text{Ir}^{\text{V}}$  intermediates thereby driving the catalytic reaction through a  $\text{Ir}(\text{III}/\text{V})$  mechanism. In view of the lack of mechanistic studies supported by computational studies on rhodium and iridium hydrosilylation catalysts, the operating mechanism has been investigated by theoretical calculations at DFT level. In addition, the mechanism of the competitive dehydrogenative silylation process has also been studied.

### References

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- [2] D. H. Nguyen, J. J. Pérez-Torrente, M. V. Jiménez, M. V.; F. J. Modrego, D. Gómez-Bautista, F. J. Lahoz, L. A. Oro, *Organometallics* **2013**, 32, 6918–6930.